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PROTON TURNOVER IN FOREST ECOSYSTEMS

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Abstract

The actual rates of proton deposition and of soil internal proton production are derived from the measurements of the fluxes of elements within a beech and a spruce forest ecosystem in the German Solling region over a period of 11 years. The following processes accounted for the soil internal production of protons:
- Accumulation of "excess.cations" in biomass
- Net production and leaching of organic and mineral acids
- Uptake of NH_4^+ and NO_3^- which entered the system by deposition
- Buffering of protons from deposition on the leaves.

The turnover of protons connected with these processes is quantified for the investigated stands and the rates of proton production caused by the accumulation of "excess cations" and by the leaching of organic acids is compared to the proton load resulting from deposition processes.
It has been concluded that more than 70 % of the total proton load (reaching up to 3.1 $keq.ha^{-1}.a^{-1}$ for the beech and to 7.0 for the spruce stand) is caused by the deposition of air pollutants.
These data emphasize the importance of acid deposition as main cause of destabilization of forest ecosystems under Middle European conditions.

INTRODUCTION

Today man influences forest ecosystems mainly in two ways: by management and by production and distribution of air pollutants. Both processes are connected with the input of protons to the ecosystem.
The soil representing the reaction vessel of the forest ecosystem has to carry the net load of these impacts which may change the chemical state of the soil in the long run. Such alterations will occur if the load of protons exceeds the buffer capacity of the soil (Ulrich 1983b).
The chemical state of the soil determines the productivity of the ecosystem as well as the composition of plants and other organisms to a large extent. This is due to the differing supply of nutrients and to the possible occurrence of soil borne toxicity.
Constant chemical properties of the soil are therefore a main condition for the long lasting stability and productivity of forest ecosystems. That is why special attention has to be given to the processes that may alter the soil

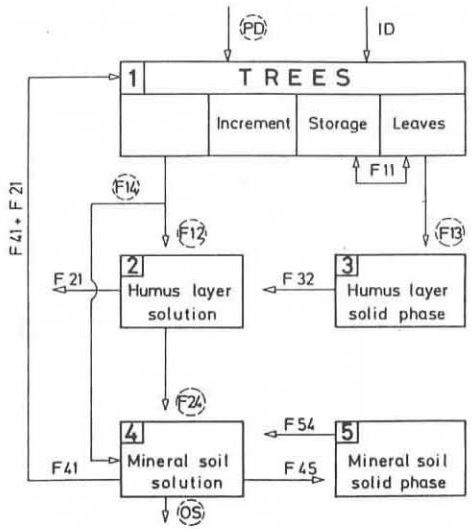
when dealing with the question: What properties give the best information of state and change of a forest ecosystem.
At present the origin and consequences of soil acidification which has been demonstrated over wide forest areas of Middle Europe are discussed controversely. Soil acidification is the result of the input or the soil internal production of protons.
Calculations of the soil internal rate of proton production in forest ecosystems were carried out by Likens et al. (1977), Andersson et al. (1980), Sollins et al. (1980) and by Nilsson (1983).
From the flux balance of a Douglas-Fir ecosystem in Western Oregon Sollins et al. (1980) concluded that the effect of acid deposition on the proton budget is negligible. Also Nilsson pointed out that under North European conditions rain water acidity is more likely to lead to stream water acidification whereas root uptake will primarily acidify the soil.
Any evaluation of the origin of soil acidification has to quantify the rates of protons from both sources. This report will focus on that by using data from measurements of element fluxes within a beech and a spruce ecosystem in North Germany.

METHODS

The data used here are obtained from the measurements of element fluxes within a 135 yr. old beech and a 100 yr. old spruce stand located in the German Solling region. The stands are described in more detail by Ellenberg (1972), while more information on the field equipment is given by Mayer (1971), Ulrich et al. (1979) and Matzner and Ulrich (1981). The annual element fluxes as well as the monthly element concentrations analysed in the various solutions are documented by Matzner et al. (1982).
The measuring approach is demonstrated by a simple compartment model of the fluxes of ions through a forest ecosystem (Fig. 1).
So far measurements of the total deposition (PD+ID) of protons and other elements in forest ecosystems over longer periods are bound to the flux balance principle. This means that the surface of the unchanged receiving ecosystem is used as a collector. The rates of total deposition of protons are then calculated from the fluxes of elements which reach the soil by canopy drip (F12) and stemflow (F14) (Ulrich 1983a).
Within a forest ecosystem the ion cycle is represented by the uptake of cations and anions into the biomass and by their subsequent release during mineralization. Both process are connected with the production or consumption of protons in the soil where these processes take place. Assuming steady state conditions, the rates of ion uptake and mineralization are equal, that is the proton turnover following mineralization is counteracted during ion uptake. In this case no effect on the chemical soil state arises from the ion cycle. Temporal and spatial discouplings of this ion cycle result in the net production of protons in the soil as shown later.
Calculations on the actual rates of soil internal net production of protons require a complete ion balance of the system. "Complete" here means that the fluxes of all major cations and anions have to be measured continuously.

Balancing the fluxes "litterfall", "canopy drip" and "input to the mineral soil", the annual rates of mineralization within the humus layer and the connected proton turnover can be calculated as well as the changes of element storage in the humus layer. Ion uptake from the humus layer (F21) was prevented by the kind of lysimeter used (living roots were cut).
Since the rates of ion uptake cannot be measured directly, they have to be calculated from the flux balance of the system. For Na, K, Ca, Mg, Mn, P and S the rates of ion uptake are assumed to be the sum of "element storage within the increment", litterfall and plant leaching. The uptake of Al and Fe results from the sum of increment and the amount of these elements which

Fig. 1: Compartment model for the fluxes of elements within a forest ecosystem



PD = precipitation-deposition
ID = interception-deposition
OS = output with seepage water

Ecosystem internal fluxes:
F11 = translocation of elements inside the plant
F12 = canopy drip
F13 = litter fall
F14 = stemflow
F24 = input to the mineral soil
F21 = uptake by the stand out of the humus layer
F32 = net mineralization
F54 = release from the soil by desorption, dissolution, weathering
F45 = Fixation in the soil by adsorption, exchange and precipitation
F41 = uptake by the stand out of the mineral soil

The element fluxes marked with dotted circles were measured directly, the others were calculated.

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are found in the young leaves (needles). The uptake of Cl was neglected because of its discrimination during ion uptake (Prenzel 1979). The rates of N uptake were determined by assuming that the rates of NH_4 and NO_3 measured in the flux "input to the mineral soil", deducting the rates of NH_4 and NO_3 output with seepage water (OS), were taken up in this ratio.

Calculations on the rates of net production of protons within the mineral soil are based on the cation-anion-balance of the changes of element storage of the major cations and anions. The electroneutrality of the solid phase of the mineral soil is maintained by the cations Na, K, Ca, Mg, Mn, Al, Fe and by

the anions SO_4, Cl and PO_4. Changes in the soil storage of exchangeable NH_4 are neglected.
A net loss of the above mentioned cations from the soil storage must either be balanced by the soil-internal production of protons or by an equivalent release of anions from the soil storage. Under these conditions, the calculated rates of proton production are caused by the following processes which can be considered as spatial or temporal discouplings of the ion cycle.
- Accumulation of "excess cations" in biomass (increment, humus layer)
- Differing amounts of uptake of NH_4 and NO_3 which entered the system by deposition
- Net production of organic (R-COOH) and mineral (H_2CO_3, HNO_3) acids
- Buffering of protons from deposition on the leaves

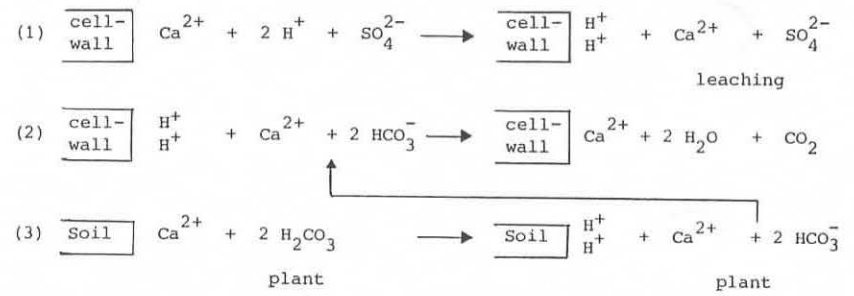
to 1: The accumulation of biomass either in form of increment or within the humus layer and the connected discoupling of the ion cycle (ion uptake exceeds mineralization) leads to a net production of protons in the soil because plants take up and accumulate more cations from the soil storage than anions ("excess cations"). That is why the "excess cations" taken up must be substituted by protons to keep up electroneutrality in the solid phase of the soil.

to 2: Significant amounts of N reach the ecosystems by deposition of air pollutants in form of NH_4 and NO_3. The annual input of N was measured for the Solling stands to about 23 $kg.ha^{-1}$ for the beech and to 30 $kg.ha^{-1}$ for the spruce stand (Matzner et al. 1982). The proportions of NH_4 and NO_3 are about the same. The input of N from the atmosphere by deposition accounts to 25 % and 40 % of the annual uptake of N of the beech and the spruce stand, respectively.
If the incoming N is taken up by the trees, proton turnover will follow: In case of NH_4-uptake equivalent amounts of protons are produced, whereas the uptake of NO_3 results in a proton consumption. If NH_4 and NO_3 are taken up in the same amount, no net production or consumption of protons will occur from the deposition of N.
By calculating the uptake of N this effect of nitrogen deposition was taken into account.
The effects of the ecosystem internal cycling of N on the proton budget can be neglected as long as no changes of NH_4 storage of the soil and no leaching of NO_3 occurrs. Under these conditions the proton turnover caused by the uptake of N is always balanced by the opposite turnover during mineralization since all N taken up stems from the mineralization of biomass. The N cycle then shows no discoupling.
That is why the ratio of NH_4/NO_3 during ion uptake should have no effect on the proton budget of the soil as long as no external input of NH_4 of NO_3 exists.

to 3: Furtheron proton production within the soil may result from the formation of organic, nitric and carbonic acids. The production of carbonic acid by root and decomposer respiration only reaches significant amounts if the pH value of the soil solution is above pH 5. Since the soil solution in the Solling stands has pH values of about 3.4 to 4.5 (according to different soil depth), proton production by carbonic acid is negligible.
Proton production as a result of nitrification becomes important when nitrate is not taken up by the plants or microorganisms (nitrification exceeds uptake of nitrate) and no denitrification takes place. In this case nitrate is leached from the soil, a process that is noticed by measuring the fluxes of nitrate with seepage water.
A specific problem in balancing ion fluxes is to include organic acids that are formed mostly during mineralization within the humus layer with subsequent transport and storage in the mineral soil. The fluxes of organic anions were

calculated from the difference of the fluxes of inorganic cations and anions. If the organic anions stored in the soil are mineralized to H_2O and CO_2 this will effect in a consumption of protons. Since no assumption can be made on the behaviour of these anions, the calculated accumulation (or mineralization) within the mineral soil was not taken into account for the whole balance.

to 4: When passing through the forest canopy protons from atmospheric deposition are partly buffered by the exchange of Ca and Mg from the cell walls of the leaves (Ulrich et al. 1979, Miller 1983, Skeffington 1983, Matzner 1983).
The following sequence of reactions will probably act during this process (Ulrich 1983c):


(1) cell-wall Ca2+ + 2 H+ + SO4 2- → cell-wall H+ H+ + Ca2+ + SO4 2-
leaching
(2) cell-wall H+ H+ + Ca2+ + 2 HCO3- → cell-wall Ca2+ + 2 H2O + CO2
(3) Soil Ca2+ + 2 H2CO3 → Soil H+ H+ + Ca2+ + 2 HCO3-
plant
plant

In the first step calcium being present in the cell walls is exchanged for protons and is afterwards leached from the leaves in connection with sulfate.

In a second reaction the protons stored in the cell walls are neutralized by HCO_3^- and the buffer is recharged by Ca. The additional uptake of Ca, connected with this process, leads in a third step to the release of protons into the soil. Hence, the protons buffered in the crowns are transferred to the soil. They reach the soil close to the root surface by the process of ion uptake instead of canopy drip and stemflow.

RESULTS

The mean annual rates of proton deposition in the Solling stands are given in Tab. 1.

Tab. 1: Annual rates of proton deposition ($keq.ha^{-1}$) (1969 - 1981)

	Beech	Spruce
Precipitation-deposition	0.8	0.8
Interception-deposition	1.2	3.2
Total deposition	2.0	4.0

Due to different rates of interception-deposition the rates of total deposition under spruce are two times higher than those of the beech stand. This observation is caused by the higher filtering area of the spruce stand and by the fact that hard-woods are leafless during winter when the rates of interception-deposition reach their maximum (Ulrich et al. 1979).

Coming back to the rates of proton production within the soil the proton producing (and consuming) processes and their rates are demonstrated in Tab. 2.

Tab. 2: Proton production within the soil (keq.ha^{-1}.a^{-1}) (1971 - 1981)

	Beech	Spruce
Accumulation of "excess cations" (increment)	0.7	1.5
Accumulation of "excess cations" (humus layer)	0.1	0.0
Uptake of NH_4 from deposition	0.9	1.1
Uptake of NO_3 from deposition	- 0.7	- 0.1
Production and leaching of organic acids	0.1	0.5
H^+ buffering on the leaves	0.6	0.9
Sum	1.7	3.9

The processes listed in Tab. 2 contribute to a different extent to the rates of proton production. The biggest part is represented in both stands by the accumulation of "excess cations" by increment. The term "increment" includes the increment of timber, barks, twigs and roots (> 5 mm) (Matzner et al. 1982). The accumulation of "excess cations" within the humus layer did not play a significant role.
The strong increase of organic matter and nitrogen storage of the humus layer during the time period from 1966 to 1979 reported by Ulrich et al. (1980) and Matzner and Ulrich (1981) under these stands was not connected with an equivalent accumulation of "excess cations". Because of low binding intensity the basic cations are released in the long run despite of accumulation of organic matter. Furtheron a slight retention of SO_4 within the humus layer was followed that counteracts the increase of the storage of "excess cations".
By removing biomass from forest ecosystems which is usually the case in managed forests, the proton consumption that would follow the mineralization of the harvested biomass is prevented with the consequence of net production of protons within the soil. The rates of proton production caused by the removal of biomass depends on the amount of biomass and on the concentrations of "excess cations" within that biomass (Nilsson 1983). If only the bole is removed, the mean annual proton production would amount to 0.5 (beech) and to 0.3 keq.ha^{-1} (spruce). The additional removal of branches would account for 0.1 and 0.3 while the harvesting of the root biomass yields in the production of another 0.1 and 0.9 keq.ha^{-1}.a^{-1} for beech and spruce, respectively.
A very different behaviour of beech and spruce becomes obvious when looking at the uptake of NO_3^- from deposition. While the beech stand is able to take up nearly the total amount of incoming nitrate, nitrate is almost complete lost from the spruce stand by the output with seepage water. As the deposited NH_4^+ is totally taken up by both stands, the net proton production caused by the uptake of N from deposition increases up to 1.0 keq.ha^{-1}.a^{-1} under spruce but only to 0.2 under beech.
The production and leaching of organic acids is negligible under beech accounting to 0.1 keq.ha^{-1}.a^{-1} while this process was measured to a rate of about 0.5 keq.ha^{-1}.a^{-1} for the spruce stand.
The rates of proton buffering in the crowns are calculated to 0.6 for the beech and to 0.9 keq.ha^{-1}.a^{-1} for the spruce stand. According to the load of

acidity being higher under spruce and to the fact that proton buffering on the spruce needles runs over the whole year, this difference could be expected.

The element balance of the soil used the fluxes of protons with canopy drip and stemflow as input instead of the rates of total deposition. Therefore the rates of proton buffering on the leaves occur as proton production in the soil.
Since the rates of proton buffering were also considered when calculating the rates of proton deposition they have to be substracted from the internal production if the sum of internal and external proton load is calculated.
The total proton load then raises up to 3.1 and 7.0 keq.ha^{-1}.a^{-1} for the beech and the spruce stand.
Assuming no deposition of N and protons, the internal proton production in the soils of these ecosystems would only account for 0.9 and 2.0 keq.ha^{-1}.a^{-1} for beech and spruce, respectively. These rates represent the real contribution of ecosystem internal processes to the total proton load of the soil.

More than 70 % of the total proton load is directly covered by the deposition of air pollutants.
If the accumulation of organic matter within the humus layer and the production and leaching of organic acids are considered as being indirectly caused by acid deposition soil acidification, this proportion would even be higher.

CONCLUSION

The total proton load found in these ecosystems exceeds by far the known rates of buffering in soils by silicate weathering and release of basic cations (Nilsson et al. 1982, Johnson et al. 1980, Bache 1982, Mazzarino 1981, 1983). The maximum values for proton consumption by silicate weathering were estimated to about 2 keq.ha^{-1}.a^{-1}. However, these rates may be overestimated since they are mostly reported from watershed studies and no correction on the possible change of the storage of exchangeable cations were made. Therefore in most forest soils derived from sedimentary rocks with low content of weatherable minerals the rates of proton buffering by release of basic cations will be below 1 keq.ha^{-1}.a^{-1}.
Under the present proton load most forest soils will therefore acidify and besides losses of nutrients the occurrence of possible toxic ions in the soil is unavoidable (Al-buffer range, Ulrich 1983b).
The proportion of the total proton load of the soil that is represented by the internal production emphasizes the importance of acid deposition as main cause of soil acidification and destabilization of forest ecosystems under Middle European conditions.
If a stable ecosystem is defined as being in a quasi steady state, which means that constant storages of ecosystem elements are found over an appropriate time period, the occurrence of soil acidification indicates a change of the system.
The rates of these changes and the processes that drive these changes forward could be monitored by a proton budget of the system.
That is why a complete ion budget and lastly the proton budget gives a good information about the state and change of a forest ecosystem.

LITERATURE

Andersson, F.T., Fageström, T. and Nilsson, S.I. 1980: Forest ecosystems responses to acid deposition - hydrogen ion budget and nitrogen/ growth model approach. In: T.C. Hutchinson and M. Havas (eds): Effects of acid precipitation on terrestrial ecosystems. Plenum Press New York, 319-334

Bache, B.W. 1982: The implications of rock weathering for acid neutralization. In: Effects of Acid Deposition, Series PM, Swedish National Environmental Protection Board.

Ellenberg, H.(ed) 1971: Integrated experimental ecology, methods and results of ecosystem research in the German Solling project. Ecological Studies 2.

Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E. and Mc Dowell, W.H. 1981: "Acid rain", dissolved aluminium and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochimica et Cosmochimica Acta 45, 1421-1437

Likens, G.E., Borman, F.H., Pierce, R.S., Eaton, J.S. and Johnson, N.M. 1977: Biogeochemistry of a forested ecosystem. Springer Verlag, 1-146

Matzner, E. und Ulrich, B. 1981: Bilanzierung jährlicher Elementflüsse in Waldökosystemen im Solling. Z.Pflanzenernähr.Bodenkd. 144, 660-681

Matzner, E., Khanna, P.K., Meiwes, K.J., Lindheim, M., Prenzel, J. und Ulrich, B. 1982: Elementflüsse in Waldökosystemen im Solling - Datendokumentation. Gött.Bodenkdl.Ber. 71, 1-266

Matzner, E. and Ulrich, B. 1983: The turnover of protons by mineralization and ion uptake in a beech (fagus silv.) and a Norway spruce ecosystem. In: B.Ulrich and J.Pankrath (eds): Effects of accumulation of air pollutants in forest ecosystems. D.Reidel Publishing Company, Doordrecht, Netherlands

Mayer, R. 1971: Bioelement-Transport im Niederschlagswasser und in der Bodenlösung eines Waldökosystems. Diss.Universität Göttingen, 1-119

Mazzarino, M.J. 1981: Holozäne Silikatverwitterung in mitteldeutschen Waldböden aus Löß. Diss.Universität Göttingen

Mazzarino, M.J., Heinrichs, H., and Fölster, H. 1983: Holocene versus accelerated actual proton consumption in German forest soils. In: B. Ulrich and J. Pankrath (eds): Effects of accumulation of air pollutants in forest ecosystems. D.Reidel Publishing Company, Doordrecht, Netherlands

Nilsson, S.I. 1983: Effects on soil chemistry as a consequence of proton input. In: B.Ulrich and J.Pankrath (eds): Effects of accumulation of air pollutants in forest ecosystems. D.Reidel Publishing Company, Doordrecht, Netherlands

Nilsson, S.I., Miller, H.G. and Miller, J.D. 1982: Forest growth as a possible cause of soil and water acidification: an examination of the concepts. Oikos 39,

Prenzel, J. 1979: Mass flow to the root system and mineral uptake of a beech stand calculated from 3-year field data. Plant and Soil 51, 39-49

Sollins, P., Grier, C.C., Mc Carison, F.M., Cormack, K.jr., and Foyel, R. 1980: The internal element cycles of an old growth Douglas fir ecosystem in Western Oregon. Ecological Monographs 50, 261-185

Ulrich, B., Mayer, R. und Khanna, P.K. 1979: Die Deposition von Luftverunreinigungen und ihre Auswirkungen in Waldökosystemen im Solling. Schriften Forstl.Fak.Univ.Göttingen, Bd. 58, 1-279, Sauerländers Verlag Frankfurt

Ulrich, B. 1981: Theoretische Betrachtungen des Ionenkreislaufs in Waldökosystemen. Z.Pflanzenernähr.Bodenkd. 144, 647-659

Ulrich, B. 1983a: Interactions of forest canopies with atmospheric constituents: SO_2, alcali and earthalcali cations and chloride. In: B.Ulrich and J.Pankrath (eds): Effects of accumulation of air pollutants in forest ecosystems. D.Reidel Publishing Company, Doordrecht, Netherlands

Ulrich, B. 1983b: Soil acidity and its relations to acid deposition. In: B.Ulrich and J.Pankrath: Effects of accumulation of air pollutants in forest ecosystems. D.Reidel Publishing Company, Doordrecht, Netherlands

Ulrich, B. 1983c: A concept of forest ecosystem stability and of acid deposition as driving force for destabilization. In: B.Ulrich and J.Pankrath: Effects of accumulation of air pollutants in forest ecosystems. D.Reidel Publishing Company, Doordrecht, Netherlands

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